

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.73 Quantum Mechanics I
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Problem Set #4

Reading: CTDL, pages 94-144.

Problems:

1. RKR and Franck-Condon. Use Robert LeRoy's programs, RKR1-16 and LEVEL16! <https://leroy.uwaterloo.ca/programs.html>

For CO, consider the $A^1\Pi$ and $X^1\Sigma^+$ electronic states. The molecular constants (in cm^{-1} units) are:

	$X^1\Sigma^+$	$A^1\Pi$
Y_{00}	0.190	-0.554
Y_{10}	2169.814	1518.24
Y_{20}	-13.288	-19.40
Y_{30}	0.01051	0.766
Y_{01}	1.931281	1.6115
Y_{11}	-0.017504	-0.02325
Y_{21}	5.487×10^{-7}	0.00159
μ	6.85620871 amu	$D_0^0(X) = 89462\text{cm}^{-1}$
T_e	65075.77cm^{-1}	$D_0^0(A) = (89462-64748)\text{cm}^{-1} = 24714\text{cm}^{-1}$
$R(X)$	0.1128323nm	$R(A) = 0.12353\text{nm}$

- A. Determine the RKR $V(x)$ potential energy curves for the CO $X^1\Sigma^+$ and $A^1\Pi$ electronic states. Use the following $G(v)$ and $B(v)$ functions

$$G(v) = Y_{00} + Y_{10}(v + 1/2) + Y_{20}(v + 1/2)^2 + Y_{30}(v + 1/2)^3$$

$$B(v) = Y_{01} + Y_{11}(v + 1/2) + Y_{21}(v + 1/2)^2$$

as input to RKR. Ask RKR to calculate turning points for $-1/2 \leq v < 15$ in steps of 0.25.

- B. Calculate overlap integrals, $\langle v' | v'' \rangle$, and Franck Condon factors for all transitions between $v'' = 0$ of the X-state to $0 \leq v' \leq 15$ of the A-state. The Franck-Condon factor is

$$q_{v',v''} = |\langle v' | v'' \rangle|^2$$

where q is the F-C factor, v' and v'' are respectively the vibrational quantum numbers for the upper (A) and lower (X) electronic states.

- C. Sketch what the A–X absorption spectrum would look like. Consider that initially only $v'' = 0$ is populated and represent each vibrational band as a vertical line, at the frequency of the $v' \leftarrow v'' = 0$ transition, with height equal to the F-C factor. [This cartoon of the spectrum ignores the rotational structure of each vibrational band.]
- D. Now create a wavepacket in the $A^1\Pi$ state by using a 1fs laser pulse, centered at $\sim 72,000 \text{ cm}^{-1}$, to *in effect* transfer the $v'' = 0$ wavefunction onto the upper potential. A 1fs pulse has a Fourier Transform width of $\sim 15,000 \text{ cm}^{-1}$.

$$\Psi(x, 0) = \sum_{v'=0,15} \langle v' | v'' = 0 \rangle \psi_{v'}(x) \quad [x = R - R_e]$$

- (i) Plot $|\Psi(x, 0)|^2$ vs. x . Compare it to $|\psi_{v''=0}(x)|^2$.
- (ii) Calculate $\langle E \rangle = E_0$, $\langle x \rangle = x_0$, and $\langle p \rangle = p_0$ at $t = 0$ for this wavepacket. You are going to have to ask LeRoy's programs to calculate a lot (136 each for E , x , and p) of integrals of the form $\langle v | \mathbf{H} | v \rangle$, $\langle v | \mathbf{x} | v \rangle$, and $\langle v | \mathbf{p} | v \rangle$. If this turns out to be too difficult, use harmonic oscillator selection rules ($\Delta v = \pm 1$ for \mathbf{x} and \mathbf{p} , $\Delta v = 0$ for \mathbf{H}) and scaling rules ($\langle v+1 | \mathbf{x} | v \rangle = (v+1)^{1/2} \langle 1 | \mathbf{x} | 0 \rangle$ and similarly for \mathbf{p}).
- (iii) Why is $p_0 \approx 0$? Why is $\langle x \rangle_0 \approx R_e(X) - R_e(A) = -0.0107 \text{ nm}$? Why is $E_0 \approx 65,076 + V_A(R = R_e(X))$?

- (iv) The classical Franck-Condon principle requires that, because an electronic transition is “instantaneous”, the nuclear coordinates and momenta do not change, $\Delta R = 0$ and $\Delta P = 0$. The $\Delta R = 0$ rule requires transitions to be vertical and the $\Delta P = 0$ rule is nearly equivalent to a requirement that strong transitions be from turning point to turning point (where $p(x) = 0$). This means that you can determine E_0 and $\langle x \rangle_0$ from a simple potential curve diagram rather than the lengthy calculation you have done in part D(ii). Compare the values of E_0 and $\langle x \rangle_0$ obtained from the potential curve diagram to those you obtained in a rigorous calculation.

E. Now set up

$$\Psi(x,t) = \sum_{v'=0,1,5} \langle v' | v''=0 \rangle \psi_{v'}(x) e^{-iE_{v'}t/\hbar}$$

for the wavepacket in part D. You have already calculated $\langle v' | v''=0 \rangle$ in part B. Be sure to retain the signs of the overlap integrals.

- (i) Compute and plot $\langle x \rangle_t$, $\langle p \rangle_t$.
- (ii) What does your plot of $\langle x \rangle_t$ tell you about the width of the upper potential, $V_A(x)$, at $\langle E \rangle_t$? [NOTE that $\langle E \rangle_t = \langle E \rangle_0 = E_0$!] What does it tell you about the shape of $V_A(x)$? What does the maximum value of $\langle p \rangle_t$ tell you about the depth of $V_A(x)$ (i.e. the energy of the minimum of $V_A(x)$)?
- (iii) $\langle x \rangle_t$ and $\langle p \rangle_t$ are not observable directly in a simple time-domain experiment. However, the average oscillation period of $\langle x \rangle_t$ of the wavepacket is easily measurable. Compare the oscillation period, T , defined as $\langle x \rangle_0 = \langle x \rangle_{T/2}$, to $\rho(E_0)/c$, where $\rho(E_0)$ is the density of states at E_0 in units of $1/\text{cm}^{-1}$ and c is the speed of light in units of cm/sec . You can obtain $\rho(E_0)$ from $\left. \frac{dG(v)}{dv} \right|_{v=v(E_0)}$ and $v(E_0)$ is obtained from

$$E_{\text{vib}} = E_0 - T_c = G(v(E_0)).$$

- F. Plot the survival probability of your wavepacket

$$P(t) = \left| \langle \Psi(x, t) | \Psi(x, 0) \rangle \right|^2.$$

You should see a series of partial rephasings, each one smaller than the previous one. Why? Will the system ever rephase nearly perfectly to $P(t) \approx 1.0$? If so, can you predict when this will occur?

- G. There is a lot of useful information in $P(t)$. The initial rate of decay of $P(t)$

is related to $\left. \frac{dV(x)}{dx} \right|_{x=x_0}$ because the force on the wavepacket is -1 times

the gradient of $V(x)$. In order to relate the initial decay rate of $P(t)$, via classical mechanics, to the gradient of the potential at x_0 , we need to define a semi-classical length of the wavepacket so that we can imagine the wavepacket moving away from perfect overlap with itself at $t = 0$ and use this to define a time-dependent overlap probability.

Use the square root of the variance of the X : $\Sigma \cdot v'' = 0$ wavefunction. You should treat this state as if it were the perfect Gaussian wavefunction that is the $v'' = 0$ eigenstate of a harmonic oscillator with $\omega_e = 2169.819 \text{ cm}^{-1}$ and reduced mass $\mu = 6.85620871 \text{ a.m.u.}$ When ω_e is in cm^{-1} units

$$(k/\mu)^{1/2} = 2\pi c \omega_e.$$

Assume that $P(t)$ has decayed to $1/2 P(0)$ when the Gaussian wavepacket has moved a distance equal to $1/2 \text{FWHM}$ of the *squared Gaussian*. If Δx^2 is the variance of $\psi_{v''=0}(x)$, then the FWHM of $|\psi_{v''=0}(x)|^2$ is

$$\text{FWHM} = 2\Delta x (\ln 2)^{1/2}$$

and the distance that the center of the wavepacket must move so that $P(t_{1/2}) = 0.5 P(0)$ is $0.833 \Delta x$. The $v'' = 0$ wavefunction

$$\psi_0(x) \propto e^{-\alpha x^2/2}$$

where

$$\alpha = (k\mu / \hbar^2)^{1/2}.$$

You can approximate $V(x)$ as linear at x_0 .

This provides a universal relationship between $\left. \frac{dV}{dx} \right|_{x_0}$ and the decay rate of $P(t)$. Using this relationship, the slope of an excited potential curve may be experimentally determined at $R_c(x)$ from the observed $\left. \frac{dP}{dt} \right|_{t=0}$.

- H. The ratio of $P(t)$ values at the second and first partial recurrences of the wavepacket, $P(T_2)/P(T_1)$, provides information about the ratio of the anharmonicity of the potential to the average vibrational frequency at E_0 . For a $G(v)$ function truncated to

$$G(v) = Y_{10}(v + 1/2) + Y_{20}(v + 1/2)^2$$

$$\rho(v) = Y_{10} + 2Y_{20}(v + 1/2).$$

Thus, for a wavepacket with average excitation energy E_0 , $P(T_2)/P(T_1)$ is going to be related to the ratio

$$\frac{\left. \frac{d^2G}{dv^2} \right|_{v=v(E_0)}}{\left. \frac{dG}{dv} \right|_{v=v(E_0)}} \approx \frac{2Y_{20}}{Y_{10} + 2Y_{20}(v + 1/2)}.$$

Since you determine $Y_{10} + 2Y_{20}[v(E_0) + 1/2]$ from the oscillation period of $P(t)$ determined in part E(iii), you can determine the anharmonicity constant from $P(T_2)/P(T_1)$. From the known values of Y_{10} , Y_{20} , and $v(E_0)$ and your empirical value for $P(T_2)/P(T_1)$, obtain a value for the universal proportionality factor relating $P(T_2)/P(T_1)$ to Y_{10} and Y_{20} .

- I. What would $|\Psi(x,0)|^2$ look like if you had started the system initially in $v'' = 1$ instead of $v'' = 0$? Would this two-lobed initial preparation make $P(t)$ have a more complicated appearance? Explain. Speculate about the evolution of $|\Psi(x,t)|^2$ for such a preparation. [HINT: think in terms of two wavepackets, each with its own values of $\langle x \rangle_0$, $\langle p \rangle_0$, and $\langle E \rangle_0$.] Can you guess what these initial values are and how the center position and momentum of these two wavepackets would sample $V_A(x)$?
2. CTDL, page 203, #1. This is a beautiful introduction to “density matrices”.

Note: Athena is MIT's UNIX-based computing environment. OCW does not provide access to this environment.

Running RKR1 and LEVEL 7.4

A Guide for the Perplexed

I. Preamble: Using the Athena FORTRAN Compiler

Download the codes from LeRoy's website. Export the code from your email reader into a text file with a .f extension (make sure you have deleted any header lines inserted by the email reader). Then compile the code with this command at the Athena prompt:

```
athena% f77 X.f
```

If compilation is successful, the Athena prompt should be returned. In your directory you will find an executable file named a.out (which, however, you are free to rename). After having constructed your input file in a text editor (e.g. Emacs), use the following string to run the code:

```
athena% a.out<inputfilename>outputfilename
```

The names and extensions of the input and output files are immaterial. If the code has run successfully, you should find in your directory an output file ('Channel 6') bearing the name you specified, as well as any additional output files ('Channel n': named fort.n) you may have called for in your input deck.

II. Running RKR1

For both programs, read carefully the listing of flags in the writeups. The Appendices of sample input and output files can be helpful, as well. For RKR1, input file sample #4 is probably the closest match to your needs (energy data read in via Dunham coefficients, though many more than you have). Notice how few lines you really need! My advice: stick to the bare essentials, and don't bother with frills. Some details, by READ line:

- 1) **Remember to include a header—it doesn't matter what it says, but there must be something here.**
- 2) Set IWR>0. You'll get a compact output of turning point data (fort.7) that is convenient for plotting and reading into LEVEL.
N.B. NVC = NRC = 3 (3 Dunham constants each for vib. and rot.)
4-7;9) These lines not required for Dunham-type input.

III. Running LEVEL 7.4

This program will generate the most confusion. **READ THE WRITEUP CAREFULLY.** You'll want to look at the sample input file #2 (potential read in as RKR turning point data; this is the companion file to RKR sample #4). But note that in the latest version, **VSHIFT has been transferred from line #5 to line #7**, with RFACT and EFACT. The sample decks do not yet reflect this. *Wherever there is a discrepancy, follow the writeup, not the samples.* Some things to watch for, by READ line:

- 3) **Remember header line here.**
- 4) Cf. Writeup re appropriate orders of magnitude for these parameters.

- 5) Set LPPOT = 0 (don't want printout of potential). VLIM: see discussion below.
 - 6) Set ILR = -1, 0 or 1. Set NCN = CNN = 0.
 - 7) VSHIFT: See discussion below.
 - 8) List turning points here. Note that it is probably easier to call the A-state potential 1, and the X-state, potential 2. Be careful to exclude any incomplete data pairs.
- 9-15) These lines not required for non-analytic potential.
- 16) Set LXPCT = -4.
 NJM & JDJR: To avoid a deluge of output, I recommend you confine your attention to $J'' = 0$ states downstairs and $J' = 1$ states upstairs (that is, only consider R(0) transitions). So set IJ (i) = NJM = 1, JDJR = 0.
 Set LPRWF < 0 to get compact wavefunction output in `fort.10`.
 - 18-19). These flags govern the form of the functions of R whose matrix elements are desired. **For matrix elements of $R = 0 + 1 * R$:**
 Set MORDR = 1, IRFN = RREF = 0
 Set DM(0) = 0, DM(1) = 1
For matrix elements of $P = -I * d/dR$ (cf. Version 7.4 Update, p. 16):
 Set MORDR = 0, IRFN = -4
 Set DM (0) = 1
 - 20-23). These lines not required.

N.B.: *If two potentials are read in, all matrix elements computed will connect levels belonging to the two different potentials.* The matrix elements of R and P which you want connect different vibrational levels of *the same potential* (A-state). Therefore, after getting F-C factors, you will have to make a second run eliminating the X-state data and setting NUMPOT = 1.

A note regarding dissociation energies: Both of these electronic states dissociate to the same asymptote! D_0^0 measures the energy gap between dissociation and the *vibrationless level* ($v=0$), *not the well minimum*. T_e measures the vertical energy gap *between potential minima*, and is the appropriate parameter to use for VSHIFT for the A-state potential.

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